

Synthesis of Hexagonal Columnar ZrB_2 Powders Through Dissolution-Recrystallization Approach by Microwave Heating Method

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Hexagonal Columnar ZrB_2 powders were obtained from irregular commercial powder at low temperature using microwave heating technique. It was confirmed that the raw ZrB_2 powders first underwent dissolution process in the glassy coating, followed by re-crystallization. A growth mechanism involving selective attachment is proposed to explain the formation of the hexagonal tubules.

I. Introduction

ZIRCONIUM diboride ceramics (ZrB_2) are used in high-temperature environments due to their high melting point and their outstanding electrical and thermal conductivities. These ceramics also possess an excellent corrosion resistance as well as a high thermal shock resistance.^{1–3} ZrB_2 ceramics are generally polycrystalline after sintering at high temperature (above 2000°C) with equiaxed or randomly oriented grains. However, some anisotropic properties such as strength, hardness, fracture toughness, and oxidation resistance have been observed for textured ZrB_2 based ceramics.^{4,5} Therefore, the performance of ZrB_2 ceramics should be enhanced by controlling the development of the grain microstructure. Messing *et al.* have comprehensively studied the synthesis and characterization of textured alumina ceramics, and pointed out that improved structural and electronic properties could be achieved when polycrystalline ceramics exhibit some anisotropic characteristics typical of single crystals.⁶ For instance, textured polycrystalline alumina fabricated via templated grain growth (TGG) had a strength and fracture toughness increased of about 62% and 48% respectively, in comparison to their counterparts with coarser grains.⁷ Besides, Wang *et al.* also observed that the alumina ceramics with a textured microstructure can achieve a high transparency (70.3% at 600 nm).⁸

In the previous investigations, two main approaches were employed to achieve the textured ceramics. The first one is the alignment of each ceramic green powder in suspension under a very strong magnetic field before sintering. The difference in magnetic torsion along different crystal axes of anisotropic crystals is responsible for the direction-selected alignment in this method. The second approach is the TGG method in which platelike ceramic powders were mixed with

precursors and sintering aids to form slurry for subsequent tape casting. The sintering of the previously tape-cast green samples induces anisotropic grain growth. One or two-dimensional ceramic seeds are the necessary prerequisites in this technique. To apply TGG method to produce textured ZrB_2 ceramics, morphology-controlled synthesis of single crystal seeds is required.

In this communication, the microwave heating method was employed to promote the formation of columnar ZrB_2 crystal in a glassy mixture of ZrO_2 , B_2O_3 and C. Nucleation and growth of uniform columnar crystals of ZrB_2 were carefully studied. It is believed that the dissolution-recrystallization growth mechanism is linked to this preferential morphology transformation of ZrB_2 crystals.

II. Experimental Procedure

Zirconium oxychloride octahydrate ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, 98%) and boric acid (H_3BO_3 , GR), were used as the sources of Zr and B, respectively. Chitosan (deacetylation $\geq 95\%$, Viscosity 100–200 mPa·s) was used as a polymerizable monomer and as carbon source. Glutaraldehyde (GR, 50% in H_2O) was used as a crosslinking agent. Commercial ZrB_2 powders with irregular morphology were used as seeds with average particle size ranging from 3 to 5 μm .

The detailed process of synthesis of columnar ZrB_2 powders is described below. Typically, 1 wt% of chitosan in acetic acid solution was prepared. Then, H_3BO_3 and $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ were added into the chitosan solution to form a transparent Zr–B–C–O precursor solution. The amounts of chitosan, $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, and H_3BO_3 were determined according to the molar ratio of C/Zr/B = 10/5.2/1. Raw ZrB_2 particles were then put into the Zr–B–C–O precursor solution and stably suspended due to the high viscosity of chitosan polymer. Glutaraldehyde was added to the suspension and kept at a temperature of 65°C for 10 min for polymerization until a stable gel formed. The obtained gel was freeze-dried, and the resultant mixture powder was pyrolyzed at a rate of 8°C/min to 800°C for 1 h in a tube furnace under a flow of nitrogen gas to allow the transformation of the Zr–B–C–O precursor into ZrO_2 , B_2O_3 , and amorphous carbon.

High-temperature boro/carbothermal reduction reaction was carried out in a high-vacuum microwave furnace (HAMiLab-HV3, SYNOTHERM co., Changsha, China) at target temperatures ranging from 1280°C to 1320°C in Ar atmosphere. The heating rate was 20°C/min below 1100°C and then 10°C/min up to the target temperature.

The phase composition of the products was identified by powder X-ray diffraction (XRD; Bruker AXS D8 Discover, Karlsruhe, Germany) with CuK_α radiation and Si as an internal standard. The morphology of the products was observed

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using scanning electron microscopy (SEM; Hitachi S-4800, Tokyo, Japan) equipped with an energy dispersive spectroscopy (EDS) system. Transmission electron microscopy (TEM; Tecnai F20, Phillip, Eindhoven, Holland) was also used to determine the phase composition.

III. Results and Discussion

The morphology of raw ZrB_2 particles and microwave-synthesized products at various temperatures are shown in Fig. 1. The commercial ZrB_2 powder particles [Fig. 1(a)] are irregularly shaped with some ZrO_2 or B_2O_3 impurities on their surfaces. After microwave heating at 1280°C , a glassy coating and worm-like particles were formed on the surfaces of raw ZrB_2 particles [Fig. 1(b)]. High-resolution TEM image shows that these oxide particles are in an amorphous state (not shown). At 1290°C , the amount of these coatings was reduced while the raw ZrB_2 particles were totally transformed into agglomerates of small grains [Fig. 1(c)]. At 1300°C , some dots and rods are visible on these small grains [Fig. 1(d)]. At 1310°C , these rods became predominant and preferentially grew together into clusters [Fig. 1(e)]. Finally, all small grains were transformed into hollow and columnar whiskers at 1320°C [Fig. 1(f)]. The average length of these whiskers is about $12\text{ }\mu\text{m}$, and the aspect ratio is about six. It is noteworthy that nearly all raw ZrB_2 powder particles have disappeared in the final product. This fact is related to the efficiency of the microwave heating method to promote the dissolution and recrystallization of ZrB_2 materials.

Figure 2 shows the XRD patterns of products synthesized by microwave heating method at different temperatures. At low temperatures such as 1280°C and 1290°C [Figs. 2(a) and (b)], ZrO_2 and ZrB_2 phases are identified. The presence of ZrB_2 phase is attributed to the raw material. A broad peak at 27° is related to the existence of carbon from the decomposition of chitosan. The glassy phase of B_2O_3 is not detected owing to its amorphous state. However, EDS

analysis on the worm-like particles [Fig. 1(b)] indicates that their main composition is ZrO_2 , B_2O_3 , and C. Seemingly, the Zr-B-C-O precursors have completely reacted and been transformed into ZrB_2 phase at temperature as low as 1320°C [Figs. 2(c) and (d)].

The morphology evolution of ZrB_2 particles from the irregular to the columnar shape, is remarkable since the shape-controlled synthesis of such covalently bonded materials has been seldom reported. Recently, Zhang *et al.* found that rod-like ZrB_2 particles can be synthesized using carbon black as carbon source.⁹ The intermediate product of B_2O_3 was regarded as a crucial factor that promotes the anisotropic growth. The molten B_2O_3 is also expected to play a crucial role for the further boro/carbothermal reduction since the reaction temperature in present work was close to that reported by Zhang (1300°C). Indeed, the glassy coating is easily observed in the products synthesized at low temperature [Fig. 1(b)]. The molten B_2O_3 phase might lower the nucleation temperature of ZrB_2 leading to the synthesis of submicron-sized or nano-sized particles.¹⁰ However, there is an unexpected reordering or an oriented growth of ZrB_2 crystals by microwave heating technique at high temperature [Fig. 1(f)]. This fact means that the molten B_2O_3 phase might have acted as a “reaction pool” favoring the atomic diffusion during crystal growth.

In the present work, the well-crystallized columnar ZrB_2 products can be attributed to the following factors. First, the uniform distribution of atomic elements in the Zr-B-C-O ceramic precursor through the gel formation technique has considerably shortened the atomic diffusion distance, thus lowered the reaction barrier. After microwave heating, the as-formed ZrO_2 , B_2O_3 and C may have transformed into an amorphous solid solution that wrap the raw ZrB_2 particles [Fig. 1(b)]. High-resolution TEM observations and selected-area electron-diffraction results (not shown) of a ceramic precursor particle have confirmed the amorphous nature of the coating. The raw irregular ZrB_2 particles might have been

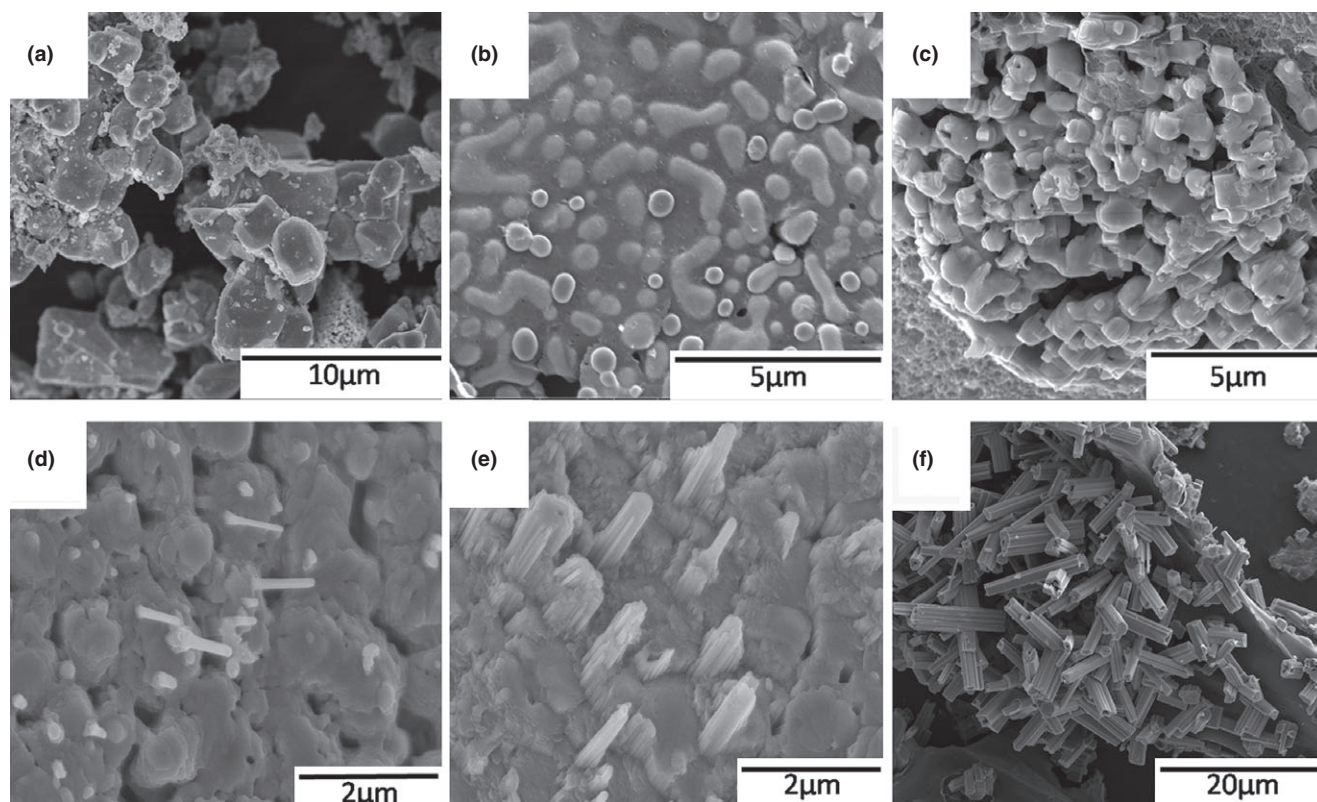


Fig. 1. The SEM images of (a) raw ZrB_2 particles and the products that were obtained by microwave heating method at (b) 1280°C , (c) 1290°C , (d) 1300°C , (e) 1310°C and (f) 1320°C for 1 h.

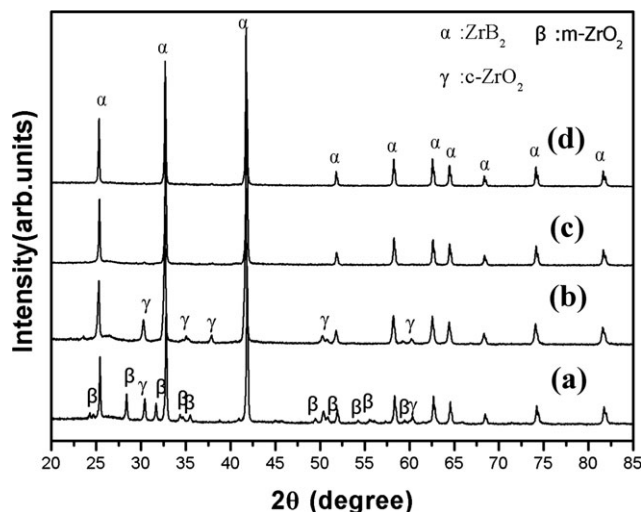


Fig. 2. The X-ray diffraction patterns of products that were synthesized at (a) 1280°C, (b) 1290°C, (c) 1300°C and (d) 1320°C.

dissolved into the amorphous solid solution since the original particles as well as the coatings gradually transformed into small particles at temperature above 1290°C [Figs. 1(c) and (d)]. Besides, the high-energy conversion efficiency of microwave heating method may have contributed to the resulting columnar ZrB_2 particles. Indeed, contrary to the traditional heating approaches (such as thermal conduction, thermal convection, and thermal radiation), microwave heating takes advantage of the electromagnetic absorption capability of target materials and allows a volumetric heating in the whole materials. ZrB_2 is a kind of conductive material, and can effectively absorb the microwave power through conductive loss mechanism. Meanwhile, the glassy solid solution coating of Zr-B-C-O is transparent to the microwave and insulated

to heat transfer. Therefore, a sharp temperature gradient might have been built up near the interface of raw ZrB_2 particles and coatings. The latter may have provided a driving force for the observed dissolution of ZrB_2 seeds into solid solution. When the concentrations of Zr and B are over-saturated, the ZrB_2 phase will nucleate and recrystallize from the solid solution [Figs. 1(d) and (e)]. It is believed that the poor microwave absorption and the low thermal conductivity of the glassy coating of Zr-B-C-O may have resulted in a moderate evaporation of B_2O_3 . This may have provided a substantial growth environment for the columnar particles of ZrB_2 .

It is interesting to note that during the recrystallization of ZrB_2 , single rod-like crystals emerged at the initial stage [Fig. 1(d)], then a cluster of rod-like crystals grew out in a mode of side by side [Fig. 1(e)]. When the recrystallization process was performed at 1320°C for only 5 min, short hollow-columnar crystals were formed [Fig. 3(a)]. Their diameter was around 0.5 μm with an aspect ratio of about 1.5. After a longer treating time (1 h at 1320°C), the diameter of ZrB_2 became larger (about 2 μm) and the aspect ratio of the column crystals was increased to about six [Figs. 1(f) and 3(b)]. For the columnar crystal growth habit, it is believed that the prismatic crystal plans should possess lower surface energies than the polar surfaces ones (Zr-terminated or B-terminated). The total surface energy of the materials system should be at the lowest level if most of hexagonal prismatic plans of ZrB_2 with the $P6/mmm$ structure are exposed. The glassy solid solution of Zr-B-C-O may have provided a suitable environment favoring the atomic diffusion and crystal growth. The hollow tube morphology of ZrB_2 can be well observed in Fig. 3(c). This is distinguishable from rod-like morphology reported by previous work.⁹ It can be assumed that the selective attachment growth mechanism played the key role during the formation of tubular rod morphology.¹¹ Actually, in the initial growth stage the tiny rods were assembled into clusters in which they shared the prismatic plans

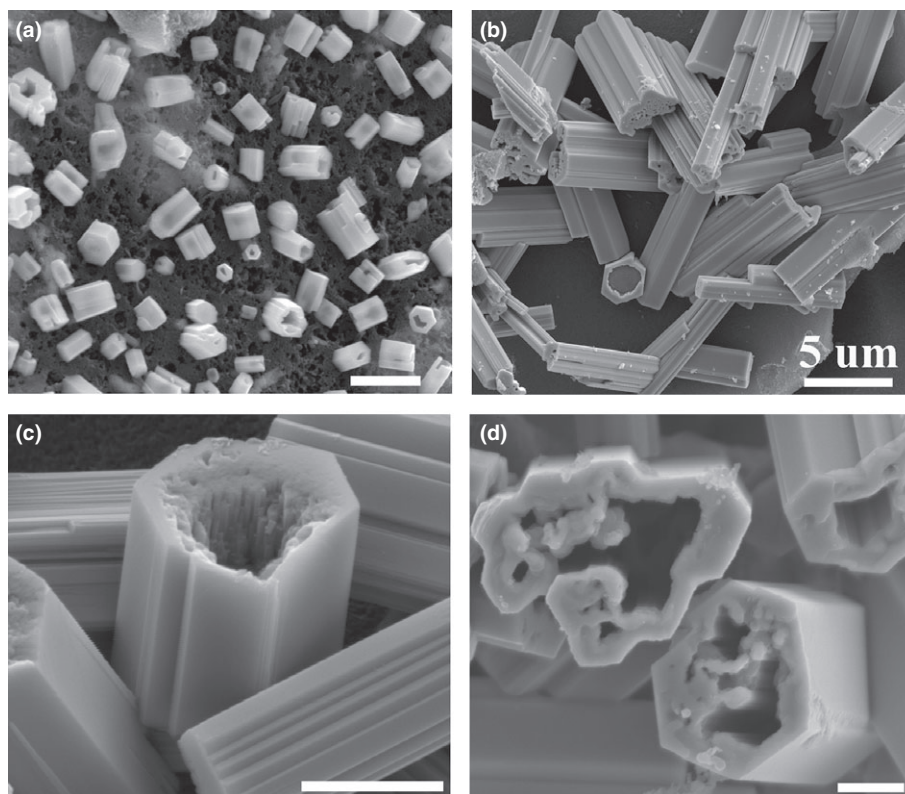


Fig. 3. SEM images showing the morphologies of ZrB_2 powders synthesized at 1320°C for (a) 5 min and (b) 1 h. (c) and (d) Enlarged images illustrating the hollow and columnar shape of ZrB_2 whiskers. The scale bars in (a), (c), and (d) are 1 μm .

[Fig. 1(e)]. This growth habit became more pervasive in the ripened columnar crystals [Fig. 3(b)]. A careful investigation of the morphology evolution from the nucleation step to the intermediate step then to the final step revealed that ZrB_2 grain growth began in the rim of the raw particles and left the holes inside of assembled rods at the final stage (Figs. 1 and 3). The diameter of final columnar crystals was almost same as that of raw particles, which corroborates the proposed tubular crystal formation mechanism by selective attachment. The ragged surface inside the whiskers may be due to the scarce feeding or difficult access of the atoms (Zr and B) in this area [Fig. 3(c)]. Few columnar crystals deviate from the strictly hexagonal shape [Fig. 3(d)], but the angles values of inside walls are close to 120° . This fact means that the formation mechanism still follows the selective attachment of pristine rods along their prismatic planes. As soon as the ZrB_2 grains nucleate and grow on the surface of Zr–B–C–O precursor ceramic particles, they should also be self-heated in the microwave field, which further enhance the growth kinetics of columnar crystals.

The as-described columnar ZrB_2 whiskers and the underlying growth mechanism may have implication for the fabrication of textured ZrB_2 ceramics as well as whisker reinforced composites. For example, the as-synthesized ZrB_2 whiskers can be added as seeds to the Zr–B–C–O ceramic precursor as the feeding source in slurry during tape casting. The long whiskers should be laid with the polar plane perpendicular to the tape surface. Thus, the TGG mechanism proposed by Messing may be applicable in the ZrB_2 material system.

IV. Conclusions

In summary, the irregular shape of commercial ZrB_2 particles was effectively transformed into hexagonal columnar shape through a microwave heating approach. A low synthesis temperature was achieved by taking advantage of the self-heating feature of ZrB_2 material under the microwave

electromagnetic field. A Zr–B–C–O ceramic precursor has provided a suitable environment for the nucleation and recrystallization of ZrB_2 particles. A selective attachment growth mechanism was proposed to explain the tubular morphology of products.

Acknowledgments

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